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(54) NOVEL PIGMENT AGGLOMERATES AND THEIR USE IN DENTIFRICES

- (71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio, 45202 United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The present invention relates to pigments in a novel agglomerate form and to processes for preparing such pigments.
- 15 The present invention also relates to dentifrice compositions, especially toothpastes, coloured in a speckled fashion with agglomerates of water-insoluble non-toxic pigment particles.
- 20 Colour has been acknowledged to play an important role in consumer acceptance of many products. In many cases, colour has been used to distinguish particular products in the market place and to identify products having particular distinct properties. Coloured products are usually formulated by merely adding the desired dye to the other components prior to the mixing stage of the process.
- 25 As the dyes currently utilized in toothpaste are all water-soluble, and varying large amounts of water are present in toothpaste, the desired colour spreads and uniformly colours the entire product. An alternative means of uniformly colouring a toothpaste is to disperse uniformly in the paste very small particles of insoluble coloured material which acts as a pigment. Although this material
- is discerned as discrete coloured particles when the paste is examined under a magnifying lens, to the naked eye the paste has a uniformly coloured appearance. For example, coloured thermosetting cross-linked resin particles can be used for uniform pigmentation of toothpastes as is disclosed in copending Application No. 31137/70 (Serial No. 1319991).
- 40 Although overall coloured effects as described above can be quite pleasing to the consumer, one of the most attractive and effective uses of colour is a speckled effect which can be achieved by incorporating a minor proportion of particles which are large enough to be readily discernible with the naked eye into a composition of contrasting colour. By uniformly dispersing such coloured particles, a product having numerous, discrete, well-defined centres of contrasting colour or colours randomly but uniformly distributed there-through, i.e. a speckled product, is obtained which presents a striking and highly distinctive appearance. While speckled toothpastes have long been known, the speckling is achieved by such substances as gold leaf and charcoal which are not really satisfactory from an aesthetic or economic standpoint. Thus, while the concept of speckling a toothpaste is old *per se*, no really effective means for executing this concept has been provided in the prior art.
- 50 The main requirements of such a speckle is that it be of sufficient size to be discernible as such; that it maintains its integrity and distinctness in the toothpaste base until the

product is used; and that it be sufficiently frangible to break up into small particles in use. Thus, it must not be susceptible to leaching, i.e. it must not bleed and colour the entire dentifrice. Since toothpastes generally contain sufficient quantities of water to cause dyes to be leached out and colour the entire product, it has not been possible to prepare speckles which are colour-fast yet sufficiently frangible to disintegrate in use so that they are not detectable in the mouth. Solid particles of the size required to produce the speckled effect generally produce an unpleasant gritty "berry seed" sensation in use, and actually become lodged between the teeth unless they break up into smaller particles when brushed upon the teeth.

The present invention provides a pigment in agglomerate form comprising particles of a water-insoluble, substantially colour-fast, non-toxic pigment bound into agglomerates of a mean size of 200 to 500 microns with a wax or gelling agent as an agglomerating agent.

Preferred particles are of a substantially water-impervious, cross-linked synthetic resin having incorporated therein a non-toxic, water-soluble dye.

The present invention further provides a process for preparing pigments of this invention wherein the agglomerating agent is a wax, which process comprises: (1) uniformly dispersing particles of a water-insoluble, substantially colour-fast, non-toxic pigment, in a molten wax; (2) cooling the wax dispersion of pigment particles to solidification; and (3) reducing the solid wax dispersion to a mean particle size of from 200 microns to 500 microns.

The present invention further provides a process for preparing pigments of this invention wherein the agglomerating agent is a gelling agent, which process comprises (1) uniformly dispersing particles of a water-insoluble, substantially colour-fast, non-toxic pigment in an aqueous dispersion of a gelling agent; (2) solidifying the dispersion to a gel; and (3) drying the gel and reducing the dried material to a mean particle size of from 200 microns to 500 microns.

The invention also provides a dentifrice composition comprising a non-toxic pigment of the invention mixed with a carrier suitable for use in the oral cavity, the pigment preferably constituting 0.05% to 2.0% of the composition. The carrier will normally be in the form of a paste.

Pigment particles which can be used to prepare agglomerates useful for speckling toothpaste in accordance with this invention are essentially colour-fast, non-toxic, and water-insoluble. The colour of the pigment particles should be of a character that the

agglomerates formed therefrom are readily distinguishable from the toothpaste base.

The primary attributes of colour are (a) hue, (b) brightness or value, and (c) saturation, purity or chroma. The hue of the particles is a matter of choice, and the preferred hue depends on the colour of the toothpaste base (a contrasting hue being necessary to secure a speckled appearance); however, using the Munsell system of colour notation (see the Munsell Book of Colour, Munsell Colour Co., Inc., Baltimore, Maryland, 1929), the particle preferably has a Munsell Value of from 4 to 7, and a Munsell Chroma of more than 4.

The pigment particles must be essentially colour-fast, i.e. must not leach a significant amount of colour in the presence of water. Thus, water-soluble dyes *per se* cannot be used in the practice of this invention. However, water-soluble dyes can be used to prepare pigment particles which will not leach colour. Colour-fast dyed thermosetting resin particles and their preparation are disclosed in copending Application No. 31137/70 (Serial No. 1319991) cited hereinbefore and such particles are preferred for use herein. Other pigment particles which can be used to prepare colour agglomerates include, for example, non-toxic, water-insoluble, inorganic pigments such as chromium oxide greens, carbon blacks, ultramarine blues and pinks, and ferric oxides; dyed cellulose particles such as dyed cotton linters and dyed wood pulp; and water-insoluble dye lakes prepared by extending calcium or aluminum salts of FD&C water-soluble dyes on alumina, such as FD&C Green NO. 1 lake, FD&C Blue No. 2 lake and FD&C Yellow No. 5 lake.

The mean particle size of the pigment particle is generally at least 5 microns, and is preferably from 10 to 200 microns. Larger particles tend to feel gritty in the mouth and stick between the teeth. The particle sizes referred to herein can be determined for example by microscopic measurements using a calibrated eyepiece.

The pigment particles can comprise from 10% to 90% by weight of the total agglomerate. Preferably, the pigment is used at a concentration in the range from 30% to 50% by weight of the total agglomerate. Pigment particles having lower Munsell Value and Chroma are preferably employed at higher concentrations.

The agglomerating agents which can be used in the practice of this invention are waxes and gelling agents. Suitable waxes are those which are non-toxic and have a hardness value of from 0 to 65 (ASTM Test D 1321-65) and preferably from 0 to 5. Examples of suitable waxes include carnauba wax, candelilla wax, purified montan wax,

castor wax, paraffin wax, ceresin wax and bayberry wax. Preferred waxes have a melting point above 70°F., more preferably from 180° to 230°F. Other waxes having these properties which can be used herein are disclosed in Soap & Chem. Specialties, Vol. 33, page 141 (1957). See also Industrial Waxes, Vols. I and II, H. Bennett, Chemical Publishing Co. Inc., New York, 1963, for a discussion of waxes and their properties.

Suitable gelling agents are those that form stable, firm dried gels which are: non-toxic; hard enough to withstand conventional shear stresses when admixed in the dentifrice or extruded from the toothpaste tube; frangible enough to disintegrate into smaller particles at time of use to give no adverse mouth impression; light coloured; innocuous in flavour and odour; and compatible with toothpaste ingredients. Gelling agents which can be used to form agglomerates of pigment particles include agar-agar, cassava starch, micro-crystalline cellulose, such as Avicel (registered trade mark) supplied by FMC Corp., and high-molecular-weight carboxy-vinyl polymers such as Carbopol 940 ("Carbopol" is a registered trade mark), supplied by the B. F. Goodrich Chemical Company.

The wax or gelling agent can comprise from 10% to 90% by weight of the total agglomerate. Preferably this component of the agglomerate is used in concentrations ranging from 50% to 70% by weight of the total agglomerate.

Agglomerates having a mean particle size of less than about 200 microns are not clearly visible as distinct species. Preferred agglomerates have a mean particle size of approximately 300 microns.

In a preferred embodiment of this invention agglomerates of pigment particles are prepared by a process which comprises the steps of (1) melting from 50 to 70 parts by weight of a wax having a hardness value of from 0 to 5; (2) uniformly dispersing from 30 to 50 parts by weight of pigment particles in the molten wax; (3) cooling the wax dispersion of pigment particles to solidification and (4) reducing the solid wax dispersion to a mean particle size within the range from 200 to 500 microns.

The wax is first heated to a temperature above its melting point in a vessel equipped with mixing apparatus. The preferred waxes for the purpose of this process have melting points within the range from 180° to 230°F. It is essential that the wax be maintained at its melting point or above when the pigment particles are added. The maximum temperature is not critical; however, it should not be so high that decomposition occurs or a fire hazard is presented.

The pigment particles are added to the

molten wax in increments which are sufficiently small to avoid a temperature drop below the melting point of the wax. Thorough mixing of the particles in the wax in molten state is necessary to ensure complete dispersion and coating of the pigment particles with wax and proper agglomeration.

After uniform dispersion of the pigment particles in the molten wax has been achieved, it is generally desirable to cool and solidify the dispersion using means which produce an easily handled solid such as by applying the molten dispersion to a drum flaker, pouring the dispersion in thin layers upon cooling trays from which the solid can be removed as flakes, or by mixing the dispersion with water and cooling same. Any method of solidifying the dispersion which yields the final agglomerates or larger pieces suitable for reduction to the final agglomerate can be used. Conventional methods suitable for this process step are described in Chapter 11 of the Chemical Engineer's Handbook, John H. Perry, 4th Ed., McGraw Hill Book Co., N.Y., 1963, under the heading "Indirect Heat Transfer Equipment for Solids". Preferably the solid dispersion is solidified to the desired size by flaking on a drum flaker.

Reduction of the solid wax dispersion to agglomerates of a desired size can be accomplished by conventional size reduction techniques described in Chapter 8, Perry's Chemical Engineering Handbook. Preferably, reduction is accomplished by a hammer mill.

It is generally desirable to screen the agglomerates after the reduction step to recover the agglomerates of the desired size (200 to 500 microns). Size classification in this manner can be accomplished by conventional techniques and equipment such as the double screen Tyler-Hummer Vibrating Sifter ("Tyler" is a registered trade mark). The agglomerates which are greater than 500 microns can be reground and the smaller agglomerates can be remelted, solidified and ground to the desired size range.

In a preferred embodiment, a dentifrice composition consists of a paste carrier having uniformly dispersed therein agglomerates of pigment particles, said agglomerates comprising (1) from 10% to 90% by weight of substantially water-impervious, cross-linked, synthetic resin particles polymerized in an aqueous solution of a non-toxic water-soluble dye and having a mean particle size of from 10 to 200 microns; and (2) the balance an agglomerating agent that is carnauba wax, candelilla wax, montan wax, castor wax, ceresin wax, bayberry wax or paraffin wax, said agglomerates comprising from 0.05% to 2.0% by weight of the toothpaste composition.

The invention is illustrated by the following Examples.

Example I

Agglomerates of green thermosetting resins suitable for speckling a toothpaste were prepared as follows:

- 5 65 parts of carnauba wax were heated to a temperature of 230°F in a melt tank equipped with a flat-blade turbine agitator. 35 parts of green thermosetting urea-formaldehyde resin particles (prepared in accordance with Example 1 of copending Application No. 31137/70 (Serial No. 1319991) were added to the molten wax with constant agitation. The particles were thoroughly dispersed in the wax and the wax dispersion was then distributed upon a drum flaker. After solidification, the flakes were pulverized in a micro-pulverizer hammer mill, and the resulting agglomerates were screened in a Tyler-Hummer Vibrating Sifter to recover those having a particle size in the range from 200 to 500 microns. The agglomerates had a Munsell Value of from 4 to 7 and a Munsell Chroma greater than 4.

- 25 Similar agglomerates are secured when paraffin wax, ceresin wax or castor wax are used in place of carnauba wax in the foregoing process. The green urea-formaldehyde resin can be replaced by particles of dyed cellulose, chromium oxide green, FD&C Blue No. 2 dye lake or ultramarine blue with comparable results.

Example II

- 35 Blue, paraffin wax agglomerates of a dye lake were prepared in accordance with this invention as follows:

- 40 To 140 parts of molten paraffin wax were added 60 parts of washed FD&C Blue No. 2 lake having a mean particle size of 20 microns. The lake particles were thoroughly dispersed in the paraffin wax and the dispersion was added slowly and with constant vigorous agitation to approximately 600 parts of water heated to a temperature of 180°F. After addition of the paraffin wax dispersion, the water was quickly cooled to 80° to 100°F by addition of cold water. The solidified coloured paraffin wax agglomerates were recovered from the water by straining the mixture through an 80 mesh screen. The agglomerates were then spread out on trays and air dried at room temperature. After drying the agglomerates were sifted through 35 mesh and 70 mesh screens. Those agglomerates which passed through the 35 mesh screen but not the 70 mesh screen were recovered for use as toothpaste speckles. The agglomerates had a Munsell Value of from 4 to 7 and a Munsell Chroma greater than 4.

- 60 Similar results are secured when bayberry wax is used in place of paraffin wax in the above process.

Example III

Dried-gel agglomerates of green urea-formaldehyde resin particles were prepared as follows:

15 g of agar and 60 of particulate, green urea-formaldehyde resin (identical to that of Example I) were added to 325 ml distilled water at room temperature. The mixture was then heated to 180°—210°F and mixed for about ten minutes. The resulting coloured gel was spread in a thin layer on a drying tray and dried in an oven at 220°F for six hours. The dried material was broken up into small pieces and pulverized. The powder was sifted as in Example II and coloured dried-gel agglomerates having a mean particle size within the range of 200 to 500 microns were recovered. The agglomerates had a Munsell Value between 4 and 7 and a Munsell Chroma greater than 4.

The urea-formaldehyde resin particles used in this example can be replaced with dyed cotton linters, dyed wood pulp, chromium oxide green, carbon black, FD&C Blue No. 2 dye lake or ultramarine pink particles of the same size with comparable results.

Example IV

Dried-gel agglomerates of chromium oxide green particles were prepared with a water-soluble polymer of acrylic acid cross linked with about 1% of a polyallyl ether of sucrose having an average of about 5.8 allyl groups for each sucrose molecule (sold under the tradename "Carbopol 940" by the B. F. Goodrich Chemical Company) as follows:

15 g of Carbopol 940 and 60 g chromium oxide green (mean particle size 20 microns) were mixed with 400 ml of distilled water at room temperature. The mixture was then heated to 180—210°F. and agitated for about 10 minutes. The resulting coloured gel was spread in a thin layer on a drying tray and dried in an oven at 220°F. for six hours. The dried material was broken up into small pieces which were then pulverized. The powder was sifted as in Example II and those dried-gel agglomerates having a particle size within the range from 200 to 500 microns were recovered. These agglomerates had a Munsell Value between 4 and 7 and a Munsell Chroma greater than 4.

The chromium oxide green in the foregoing example can be replaced with coloured melamine-urea-formaldehyde, melamine-formaldehyde or phenol-formaldehyde resin, these being as prepared in accordance with copending Application No. 31137/70 with comparable results.

Example V

Cassava starch dried-gel agglomerates of blue urea-formaldehyde resin particles were

- prepared by mixing 70 g of cassava starch and 180 g of blue urea-formaldehyde resin (particle size from 10 to 420 microns) with 400 ml of distilled water and forming agglomerates thereof in accordance with Examples III and IV. The agglomerates thus formed had a mean particle size of from 200 to 500 microns, a Munsell Value of from 4 to 7 and a Munsell Chroma greater than 4.
- 10 Toothpastes usually contain a cleaning and polishing agent, a humectant, a suds-forming agent, a binder, a sweetener, flavouring ingredients and water. The combination of such conventional components is referred to herein as the toothpaste base. Agglomerates prepared in accordance with the foregoing examples can be incorporated into toothpaste base (which acts as a carrier for the agglomerates) at any point in the mixing of these components using conventional means.
- 20 Several toothpastes speckled with the agglomerates of this invention are shown in the following examples.

EXAMPLE VI

A toothpaste was prepared having the following composition:

	% By Weight
Calcium pyrophosphate	40.79
Sorbitol (70% aqueous)	20.39
Glycerine	10.19
Sodium coconut monoglyceride sulphonate	0.76
Sodium carboxymethylcellulose	1.2
Sodium coconut alkyl sulphate (20% active)	2.29
Sodium fluoride	0.22
Sweeteners and Flavour	1.14
Green urea-formaldehyde agglomerates*	0.65
Water	Balance

* Prepared in accordance with Example I.

- 25 The toothpaste of this example had a distinctive green speckled appearance. The urea-formaldehyde agglomerates remained intact and colour-fast through the mixing procedure and storage. When extruded from a toothpaste tube upon a toothbrush the paste maintained its speckled appearance but the agglomerates readily disintegrated when the paste was brushed upon the teeth and produced no unpleasant gritty feel in use.
- 30 Several additional toothpaste compositions were prepared which were identical in formulation to that of Example VI but containing the agglomerates set forth in Table 1 below in place of the green urea-formaldehyde agglomerates:

TABLE 1

Example No.	Agglomerating Agent	Pigment	Preparation Method
VII	Arco Tuffin 30**	Urea formaldehyde*	As in Ex. I
VIII	Carnauba wax	Chromium oxide green	As in Ex. I
IX	Carnauba wax	Dyed cotton linters	As in Ex. I
X	Carnauba wax	Dyed wood pulp	As in Ex. I
XI	Ceresin wax	Urea-formaldehyde*	As in Ex. I
XII	Agar-agar	Urea-formaldehyde*	As in Ex. III
XIII	Cassava starch	Urea-formaldehyde*	As in Ex. V
XIV	Avicel	FD & C Green No. 1 Lake	As in Ex. IV

* Prepared in accordance with Example I of copending Application No. 31137/70 (Serial No. 1,319,991).

** Arco Tuffin 30 ("Arco" is a registered trade mark) is a blend of petroleum waxes and has an ASTM Hardness Value of 30. It is a product of Atlantic Richfield Oil Company.

Each of the toothpastes of the foregoing examples had properties similar to those of Example VI except that the colour of the speckling varied with the colour of the particles.

WHAT WE CLAIM IS:—

1. A pigment in agglomerate form comprising particles of a water-insoluble, substantially colour-fast, non-toxic pigment bound into agglomerates of a mean size of 200 to 500 microns with a wax or gelling agent as an agglomerating agent.
2. A pigment according to claim 1 wherein the particles have a mean size of at least 5 microns.
3. A pigment according to claim 1 wherein the particles have a mean size of from 10 to 200 microns.
4. A pigment according to any of claims 1 to 3 wherein the agglomerates have a mean size of approximately 300 microns.
5. A pigment according to any of claims 1 to 4 wherein the pigment particles constitute from 10% to 90% by weight of the agglomerates.
6. A pigment according to claim 5 wherein the pigment particles constitute from 30% to 50% by weight of the agglomerates.
7. A pigment according to any of claims 1 to 6 wherein the particles have a Munsell Value of from 4 to 7 and a Munsell Chroma of greater than 4.
8. A pigment according to any of claims

1 to 7 wherein the particles are particles of a substantially water-impervious cross-linked synthetic resin having incorporated therein a non-toxic, water-soluble dye.

9. A pigment according to claim 8 wherein the synthetic resin is a copolymer of melamine and formaldehyde.

10. A pigment according to claim 8 wherein the synthetic resin is a copolymer of melamine, urea, and formaldehyde.

11. A pigment according to claim 8 wherein the synthetic resin is a copolymer of urea and formaldehyde.

12. A pigment according to claim 8 wherein the synthetic resin is a copolymer of phenol and formaldehyde.

13. A pigment according to any of claims 1 to 7 wherein the particles are particles of chromium oxide green, carbon black, ultramarine blue, ultramarine pink, dyed cellulose or water-insoluble lakes of non-toxic dyes.

14. A pigment according to any of claims 1 to 13 wherein the agglomerating agent is a wax that has a hardness value of from 0 to 65.

15. A pigment according to claim 14 wherein the wax has a hardness value of from 0 to 5.

16. A pigment according to any of claims 1 to 15 wherein the agglomerating agent is a wax that has a melting point of above 70°C.

17. A pigment according to claim 16 wherein the wax has a melting point of 180° to 230°F.

18. A pigment according to any of claims 1 to 13 wherein the agglomerating agent is

carnauba, castor, candelilla, ceresin, bayberry, paraffin or purified montan wax.

19. A pigment according to any of claims 1 to 13 wherein the agglomerating agent is a gelling agent selected from agar-agar, cassava starch, microcrystalline cellulose or a high-molecular-weight carboxyvinyl polymer.

20. A pigment according to claim 1 substantially as hereinbefore described in the Examples.

21. A process for preparing a pigment according to any of claims 1 to 18 wherein the agglomerating agent is a wax which process comprises: (1) uniformly dispersing particles of a water-insoluble, substantially colour-fast, non-toxic pigment in a molten wax, (2) cooling the wax dispersion of pigment particles to solidification, and (3) reducing the solid wax dispersion to a mean particle size of from 200 microns to 500 microns.

22. A process for preparing a pigment according to any of claims 1 to 13 and 19, wherein the agglomerating agent is a gelling agent, which process comprises (1) uniformly dispersing particles of a water-insoluble, substantially colour-fast, non-toxic pigment in an aqueous dispersion of a gelling agent; (2) solidifying the dispersion to a gel; and (3) drying the gel and reducing the dried material to a mean particle size of from 200 microns to 500 microns.

23. A process for preparing a pigment in agglomerate form, substantially as herein-

before described in the Examples.

24. A pigment when prepared by a process according to any of claims 21 to 23.

25. A dentifrice composition comprising a pigment according to any of claims 1 to 20 and 24 mixed with a carrier suitable for use in the oral cavity.

26. A dentifrice composition according to claim 25 wherein the pigment constitutes 0.05% to 2.0% by weight of the composition.

27. A dentifrice composition consisting of a paste carrier having uniformly dispersed therein agglomerates of pigment particles, said agglomerates comprising (1) from 10% to 90% by weight of substantially water-impervious, cross-linked, synthetic resin particles polymerized in an aqueous solution of a non-toxic water-soluble dye and having a mean particle size of from 10 to 200 microns; and (2) the balance an agglomerating agent that is carnauba wax, candelilla wax, montan wax, castor wax, ceresin wax, bayberry wax or paraffin wax, said agglomerates comprising from 0.05% to 2.0% by weight of the tooth-paste composition.

28. A dentifrice composition substantially as hereinbefore described in the Examples.

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